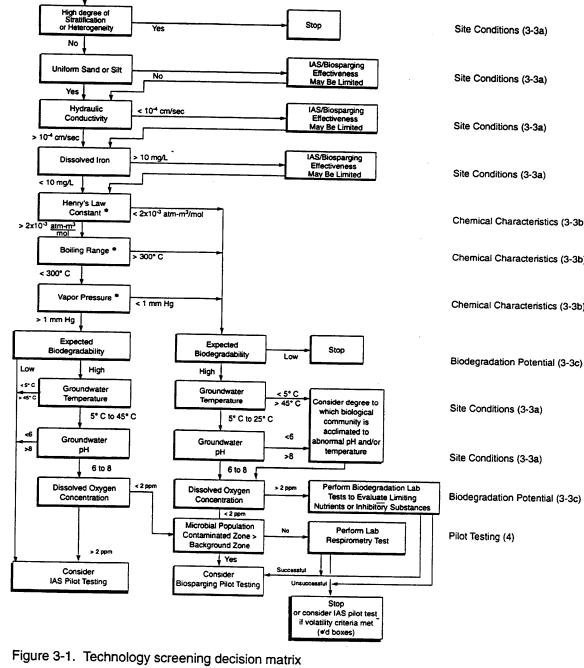
#### CHAPTER 3

### SITE CHARACTERIZATION AND FEASIBILITY EVALUATIONS

- 3-1. <u>Introduction</u>. Prior to selecting IAS for implementation, the site characteristics and the nature and extent of contamination must be assessed to evaluate the feasibility of IAS. A suggested strategy for technology screening is presented in this section, as well as pre-design data collection requirements and feasibility studies. Critical data requirements include physical, chemical, and biological properties of site media and contaminants. An example format for a Sampling and Analysis Plan (SAP) is presented in EM 200-1-3.
- 3-2. <u>Technology Screening Strategy</u>. It is advisable to perform technology screening as early in the process as possible, preferably concurrent with site characterization. Early evaluation of the data needs for remedy selection (and design) may reduce the need for subsequent mobilization to the field during design. Those undertaking technology screening must have a sense of the overall remedial objectives, some knowledge of the nature and extent of contaminants at the site, and a good grasp of the range of technologies available and their limitations. Figure 3-1 presents a decision matrix for IAS technology screening.

## a. Remediation Objectives.

- (1) At present, although there are a large number of sites at which practitioners have applied IAS, there are relatively few well-documented IAS projects that have attained closure. (The USACE has successfully closed IAS sites at Ft. McCoy, WI and the Sacramento Army Depot, CA.) Estimates of the amount of time required to operate such systems to completion are inherently uncertain, depending heavily on site specific conditions and site specific cleanup goals. The closer initial concentrations are to the target concentrations, the shorter the duration of treatment needs to be. IAS may not achieve MCLs at a site, but may be able to reach acceptable cleanup criteria negotiated on a site specific basis. Guidance for the development of site specific target levels can be found in ASTM E 1739-95 el, "Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites".
- (2) More intensive operations, such as higher well densities and higher air injection rates, may also reduce remediation time. In general, however, IAS should not be regarded as a rapid technology. Depending on how low the target concentrations must be, one if not several years of IAS may be required at well-suited sites.
- (3) The range of contaminant loadings over which IAS has been effective is also not well-defined. It is unclear whether IAS is effective at remediating sites containing large amounts of NAPL (and especially DNAPL); however, it may enhance the final LNAPL removal rate for sites where free-product recovery has been conducted, because of the effects of air movement impinging upon the capillary fringe.



- b. Influence of pattern of contamination on technology screening strategy.
- (1) A brief description of a "typical" organic loading profile in the subsurface will help in understanding the remediation objectives which are achievable using IAS, and therefore in conducting technology screening. For most sites where groundwater has been impacted by spilled or released hydrocarbons, they flow through a vadose (unsaturated) zone under the influence of gravity, until they encounter the capillary fringe. Since the water table typically rises and falls due to seasonal changes or precipitation events, the hydrocarbons become "smeared" across the capillary fringe and the water table (piezometric surface). Much of this mass is occluded in interstitial and pore spaces as small droplets of NAPL, which can only be removed by dissolution in groundwater under normal conditions. This is a very slow process, and is limited by the constituents' solubility, its diffusivity in water, and the velocity of groundwater movement. The amount of occluded NAPL is affected directly by the distribution of pore and particle sizes within the soil.
- (2) A portion of the hydrocarbons that come out of solution below the water table will partition to natural organic carbon (expressed as total organic carbon, TOC). This can add to the depth of the "smear" zone, not uncommonly creating a zone 2.5 to 3m (eight to ten feet) in thickness where most of the hydrocarbon is present, whether as small droplets of NAPL or sorbed to the soil. The amount of hydrocarbon actually dissolved in the groundwater is usually less than a few percent of the total hydrocarbon mass. Any process which solely treats the groundwater is thus required to wait for sorbed material or NAPL to dissolve.
- (3) Inasmuch as IAS creates flow paths for an immiscible (vapor) phase to move through the water, it may serve as a gentle mixer, potentially accelerating hydrocarbon transport. Since IAS also provides oxygen to the groundwater under most applications, the rate of aerobic biodegradation below the water table will also be enhanced. So while IAS is relatively slow compared to excavation-based approaches, it can be considerably faster than approaches which merely pump water and treat it at the surface. There are sites, however, where pump-and-treat is quite effective and where IAS was ineffective (R.L. Johnson, Personal Communication, 1997).
- (4) If IAS is successful mixing the groundwater and increasing hydrocarbon transport, then the groundwater quality may initially deteriorate due to increased contaminant dissolution and/or mobilization of residual NAPL. These effects will be ameliorated over time as contaminant mass is removed from the aquifer and remediation proceeds.
- (5) Recognizing how NAPL and hydrocarbons, both dissolved and sorbed, are distributed in the subsurface and how they can potentially be affected by IAS processes are prerequisites to identifying the data collection needs, as discussed in the following paragraphs.
- 3-3. <u>Pre-Design Data Collection Requirements</u>. Prior to the development of an air sparging design, physical, chemical/biological, and hydrogeologic data are needed. This information will be used to provide insight regarding the

feasibility of air sparging as a remediation alternative, as well as provide a basis for the design. Much of the required data can be collected during the investigative phase of the project. Collecting this data prior to conducting the pilot study serves two purposes: 1) it limits the need to remobilize to the site to collect supplementary site data prior to the full-scale design, and 2) the data collected may be used to guide the design of the pilot test so that the results lead more directly to a successful full-scale design. A series of characterization data parameter lists is presented in Tables 3-1 through 3-3. The text in this section provides a description of these parameters and their influence on the overall IAS design.

## a. Physical Properties and Site Conditions.

- (1) The physical characteristics of a site are critical to assessing the feasibility of IAS and subsequently designing pilot- and full-scale systems. In addition to understanding the characteristics of the saturated (i.e., sparging) zone, the characteristics of the vadose zone are also of importance to the performance of IAS. The physical properties of the vadose zone impact the dispersion of gas above the water table and the ability to effectively contain and capture it for treatment, recirculation, or exhaust.
- (2) The physical properties of the saturated zone dictate the distribution of injected gas during IAS implementation. Pertinent physical parameters are presented in Table 3-1. Useful chemical and biological property data are discussed in paragraphs 3-3b and 3-3c, respectively. Table 3-1 includes the type of sample required (i.e., collection method) and associated analytical method.
- (3) A thorough understanding of site stratigraphy is of the utmost importance. For that reason, at least one borehole shall be continuously logged and representatively sampled to the depth of the deepest sparge well to ensure that a full geologic profile is characterized. The personnel responsible for logging the borings shall be instructed to record a detailed and systematic stratigraphic sequence. Even minor changes in soil texture or porosity are significant because they can control air entry and airflow. Visual observations of soil boring characteristics, such as mottling, discoloration, and texture, as well as apparent moisture and grain size, can provide useful information. These observations can indicate groundwater fluctuations, seasonal variations, and hydraulically impeding or confining strata, such as clay lenses.
- (4) In addition to collecting soil samples for analyses of physical properties, a review of available site maps and visual inspection is recommended to better understand the site at which IAS is being considered. The presence and structure of building foundations, basements, reinforced earth, subsurface utilities and drainage structures, existing monitoring wells, soil gas monitoring points, and soil borings, filled excavations, and surface paving materials may impact the operation of an IAS system.

TABLE 3-1
Physical Parameters for Soil

Parameter	Sample Type	Analytical Method
Air-phase permeability (of saturated zone soil)	In situ or undisturbed soil Various <sup>1</sup> sample	
Grain size distribution	Split spoon or other soil sample	ASTM D422-63 (1990)e
Porosity	Undisturbed 50 to 75 mm diameter soil sample	Calculated from dry bulk density and particle density
Dry bulk density	Undisturbed 50 to 75 mm ASTM D2850-95e1 diameter soil sample	
Moisture content (of saturated zone soil)	Non-destructive field measurement; grab sample; or undisturbed 50- to 75- mm diameter soil sample	Neutron access tube measurements (Gardner 1986); ASTM D2216-92
Soil moisture retention (capillary pressure-saturation curve); Airentry pressure	Undisturbed 50- to 75-mm diameter soil sample	Klute (1986); ASTM D2325-68(1981)e1; Jones et al. 1980
Stratigraphy/ heterogeneity	Soil boring	Visual observation; Breckenridge et al. 1991; USEPA 1991; ASTM D 2488-93; EM 1110-1-4000
Depth to groundwater and range of fluctuation; hydraulic gradient and flow direction	Water table monitoring wells	Water level meter or interface gauge and surveyed well elevations; ASTM D 4750-87(1993)e1 (ensure that the probe weight is inert)
Flow paths in saturated soil	In situ field measurement	Groundwater tracer (USEPA 1985)

# TABLE 3-1 (Cont'd)

# **Physical Parameters for Soil**

Parameter	Sample Type	Analytical Method
Hydraulic conductivity	Field measurement	ASTMs: D4043-91; D4044-91; D4050-91; D4104-91; D4105-91; D4106-91; D5269-92; and D5270-92

## Notes:

<sup>&</sup>lt;sup>1</sup> USACE "Soil Vapor Extraction and Bioventing" Engineer Manual (EM 1110-1-4001), November 30, 1995

- (5) Subsurface structures in the vadose zone may alter the distribution of airflow generated during IAS and result in uncaptured offgas if left uncontrolled. For sites where little or no surface paving exists (i.e., soil or gravel surfaces), it may be difficult to capture offgas for controlled treatment, recirculation, or exhaust. Further, subsurface zones of enhanced permeability (e.g., a gravel pipeline trench or backfill or improperly abandoned soil borings and monitoring wells screened across the water table) can cause preferential channeling of air flow and limit the effective ZOI. Not only would preferential pathways reduce the interstitial air/water surface area, but the majority of subsurface contaminants may be bypassed in the event of sparsely distributed channels. Similar influences exist within the saturated zone. For example, improperly abandoned soil borings or monitoring wells can cause preferential migration of air pathways both below and above the water table surface. By properly assessing the physical conditions and heterogeneity of the subsurface prior to implementing IAS, these occurrences can be minimized or avoided.
- (6) Soil Sample Collection. Representative undisturbed soil cores shall be collected and submitted for physical parameters analysis from every major stratigraphic unit between the seasonal high water table elevation and the anticipated lowest elevation of sparge screens. Undisturbed soil samples are typically collected using Shelby-tube samplers. Samples should be collected from depth-discrete intervals for acquisition of data from various stratigraphic layers. In conditions where cobbles and boulders impede the ability to push Shelby tubes into the subsurface, representative cores may not be obtained unless a technique such as Roto Sonic® drilling is employed. Roto Sonic® drilling is an innovative vibratory dual-tube direct push method that has proven capable of collecting intact cores while achieving high penetration rates in a wide range of conditions.
- (a) It is sometimes difficult to collect undisturbed samples from the saturated subsurface with Shelby-tube samplers, because wet, non-cohesive soil may not be retained in the sampling device. Lined split-spoon samplers are recommended in this situation. When using a split-spoon sampler, brass or stainless steel liners tend to provide a more watertight seal than acetate liners. Once samples are brought to the surface, plastic end caps and end packers are effective in capping the ends of a liner prior to transport. It should be noted that the density of soil within the split-spoon liner will likely be greater than the true in-place density because compression occurs while advancing the split-spoon. In order to collect a relatively undisturbed sample in saturated sands, a 1.5-m continuous core barrel sampler (i.e., liner) placed inside the auger is recommended. In the event that soft cohesive or non-cohesive soils are encountered, equipment such as the Waterloo sampler, that uses a piston plug to create a vacuum on the sample barrel, helps ensure that saturated sands remain within the core barrel during sampling.
- (b) Analytical sampling methods are prescribed in EM 200-1-3, Requirements for the Preparation of Sampling and Analysis Plans. A detailed discussion of the effect of physical characteristics on subsurface air flow is contained in EM 1110-1-4001. Soil parameters that have effects that are specific to IAS are discussed below.

- (c) Porosity and permeability affect the degree of groundwater mounding and upwelling that may occur during pilot-scale testing and IAS implementation. Generally, the degree of mounding and upwelling is smaller under conditions of high subsurface porosity and permeability. Mounding, upwelling, and other potential start-up occurrences are further discussed in paragraph 2-7a.
- (d) Soil moisture retention data (Table 3-1) provide a means to determine the air-entry pressure of a given soil. A soil's air-entry pressure is a critically important property for IAS. More detail on the importance of air-entry pressure is provided in paragraph 2-6. Descriptions of the method of measuring air-entry pressure and interpretation of the measurements are provided below.
- (7) Moisture retention analysis for determining air-entry pressure Moisture retention analysis (ASTM D 2325-68(1981)e1) is a laboratory procedure that involves the stepwise application of a pressure differential to an initially saturated soil sample, with the equilibrium moisture content measured at each step. The first step involves application of the lowest (e.g., 33 mbar) pressure step to the sample, which induces drainage of water from the largest pores of the sample until equilibrium is approached at that pressure, at which time the sample is weighed to determine the volume of water desorbed from those pores. Then the next higher pressure is applied, inducing drainage from the next smaller class of pores, and reequilibration is allowed to occur, followed by reweighing. The process thus proceeds in a stepwise fashion, until the sample is virtually dry.
- (a) The resulting data are plotted in the form of capillary pressure head as a function of saturation (or equivalently, matric suction as a function of moisture content). A minimum of seven separate pressure points is recommended in order to ensure that the curve encompasses the most crucial moisture characteristics.
- (b) Figure 3-2 presents data from moisture retention analyses, expressed as capillary pressure head vs. moisture content, for adjacent soil cores collected from the same soil boring. The shallower, siltier sample (Figure 3-2a) has an air-entry pressure head of approximately 370 cm  $\rm H_2O$ , while the air-entry value for the deeper, sandier sample (Figure 3-2b) is approximately 36 cm  $\rm H_2O$ . Clearly, if the IAS screen intercepted both soil layers, air entry would occur into the deeper horizon first; air might not enter the shallower horizon at all.
- b. Chemical Analyses. During site characterization, the chemical properties of site media and the nature and extent of contamination must be assessed to evaluate the feasibility of IAS. As discussed in paragraph 2-11, contaminants generally amenable to IAS are VOCs, including the lighter fuels (e.g., gasoline, diesel, and jet fuel) and petroleum-related compounds, as well as cleaners, solvents, degreasers, and associated chemicals. In addition to the partitioning and removal of VOCs through stripping, IAS can be used to enhance or induce other contaminant transfer mechanisms, such as precipitation and biodegradation. As such, it is critical to acquire sufficient chemical

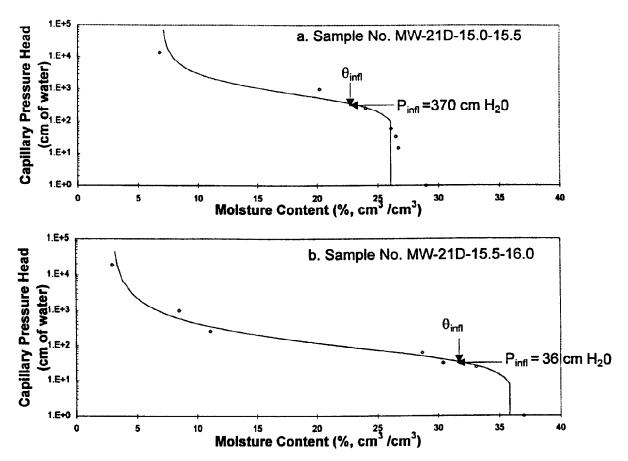


Figure 3-2 (a-b). Capillary pressure head vs. moisture content ( $\theta$ ) for two adjacent soil horizons. Intact cores collected from adjacent soil layers within the sparge zone were submitted for laboratory analysis (data points); curves are Van Genuchten (1980) functions fitted to the data. The inflection point ( $P_{infl}$ ) for the deeper, sandier layer sample (b) was found to correspond closely to the air entry pressure measured during IAS, indicating that sparged air flows preferentially within that layer, and does not even enter the shallower, siltier layer (sample a), which has a much higher  $P_{infl}$  value (Baker et al. 1996).

data to fully assess the potential for the desired IAS mechanism(s). A list of relevant groundwater chemical parameters is presented in Table 3-2.

- (1) Field Screening. A variety of field screening techniques are available for the preliminary assessment of site media. Readily available portable organic vapor analyzers include photoionization detectors (PIDs) and flame ionization detectors (FIDs). These devices provide an indication of the total organic vapor in ambient air or within the headspace of boreholes or sampling containers by comparing the vapor reading of the sample to the calibrated value of a specific compound, for either the photoionization potential of a specific lamp energy (for PIDs) or a flame ionization potential (for FIDs). If specific vapor-phase chemicals are of interest, direct-reading colorimetric indicator tubes, such as Draegger® tubes, provide useful data that may be correlated with gas chromatograph/mass spectrometry (GC/MS) analyses (NIOSH 1985).
- (a) One commonly applied method of field screening for VOCs is a soil gas survey. VOCs amenable to IAS are also generally amenable to field soil gas measurement. Soil gas surveys are useful in assessing the relative concentrations of the VOCs of interest and related compounds, as well as oxygen, carbon dioxide, and methane. The concentration of total organic vapor in soil gas can be used to estimate the initial concentration in the IAS vapor emissions. Soil gas surveys can also be instrumental in locating the soil contamination and guiding the placement of IAS and SVE wells.
- (b) Soil gas surveys can be misleading, however. For example, soil gas concentrations of specific chemicals often do not usually correlate well with laboratory analyses of soil samples. Soil gas surveys measure chemicals in the vapor phase at a given spatial point. Advection due to barometric pumping can cause vapors to travel and be detectable at a distance from source areas. Conversely, "hot spots" identified by laboratory analysis of soil samples may be present in low permeability portions of a site that are not conducive to vapor transport and therefore may not be detected during a standard soil gas survey. Thus, there is no consistent relationship between the presence of vapor-phase VOCs at a survey point and the distance from which the VOCs originally emanate (Downey and Hall 1994). Chemical-specific results of field soil gas measurements are best viewed as screening data, depicting general locations of increased vapor-phase VOCs in the vadose zone.
- (c) The shallow subsurface migration of vapor-phase VOCs (revealed by areas of increased soil gas concentrations) may be used to predict the migration of future VOCs that will be generated during IAS. This information is useful in selecting locations for confirmatory soil and groundwater samples, as well as the placement of SVE components (if required).
- (d) Vapor-phase VOCs are typically measured with a gas chromatograph equipped with an FID, PID, electron capture detector (ECD), or MS detector. Methods typically employed for collection of soil gas are listed below. In general, Standard SW 846 methods apply (USEPA 1986).
  - Adsorption onto a sorbent medium, such as charcoal, Tenax®, or Ambersorb®, followed by thermal or solvent desorption.

TABLE 3-2
Chemical Parameters for Groundwater

Parameter Preservative		Analytical Method
Biological Oxygen Demand (BOD)	4°C	SM 5210B; EPA 405.1
Chemical Oxygen Demand (COD)	pH <2 with H <sub>2</sub> SO <sub>4</sub> ; 4°C	SM 5220D; EPA 410.1
Alkalinity	4°C	SM 2320B; EPA 310.1; field measurement <sup>1</sup>
Total Dissolved Solids	4°C	SM 2540C; EPA 160.1
Total Organic Carbon (TOC)	pH <2 with H <sub>2</sub> SO <sub>4</sub> ; 4°C	SW 846 Method 9060
Iron (total and field-filtered)	pH <2 with HNO <sub>3</sub> ; 4°C	SW 846 Method 6010; field measurement <sup>1</sup>
Ammonia-nitrogen	pH <2 with H <sub>2</sub> SO <sub>4</sub> ; 4°C	SM 4500; EPA 350.1
Total Kjeldahl Nitrogen	pH <2 with H <sub>2</sub> SO <sub>4</sub> ; 4°C	SM 4500; EPA 351.2
Nitrite and nitrate	pH <2 with H <sub>2</sub> SO <sub>4</sub> ; 4°C	SM 4500; EPA 353.2; field measurement <sup>1</sup>
Sulfate	4°C	SW 846 Method 9038
Sulfides	4 drops 2N zinc acetate per 100 ml; pH >9 with 6N NaOH; 4°C	SW 846 Method 9030; field measurement <sup>1</sup>
VOCs	pH <2 with 1:1 HCl; 4°C; no headspace	SW 846 Methods 8260 or 8010/8020
SVOCs	4°C	SW 846 Method 8270
Total petroleum hydrocarbons (diesel range organics)	4°C	SW 846 Modified Method 8100; field measurement <sup>2</sup>
Depth to free NAPL phase	Direct push "soil boring", e.g. cone penetrometer <sup>3</sup>	Laser Induced Fluorescence (USEPA 1997); ETL 1110-1-171
рН	none	Field measurement⁴
Temperature	none	Field measurement <sup>4</sup>
Dissolved oxygen (DO)	none	Field measurement <sup>1, 4</sup>
Conductivity	none	Field measurement <sup>4</sup>

# TABLE 3-2 (Cont'd)

# **Chemical Parameters for Groundwater**

Parameter	Preservative	Analytical Method
Redox potential (Eh)	none	Field measurement <sup>4</sup>

SM is APHA-AWWA-WEF 1992; SW 846 is USEPA 1986 and Updates promulgated in 1992 and 1994. Refer to EM 200-1-3 for sample bottle requirements.

<sup>&</sup>lt;sup>1</sup>Alkalinity, ammonia, iron (total and dissolved), nitrate, nitrite, sulfides and DO can be determined using CHEMETRICS® field test kits (colorimetric or titrimetric methods). Each kit is prepared for single use measurement at the factory. Preservation is not applicable.

<sup>&</sup>lt;sup>2</sup>TPH (DRO) can be determined in the field using an immunoassay test kit. Preservation is not applicable.

<sup>&</sup>lt;sup>3</sup>Readers are advised to check the availability of USACE's cone penetrometer units for their projects (paragraph 3-3b(3)).  $^4$ Temperature, DO, conductivity and Eh can be determined in the field using appropriate field

- Cryogenic trapping.
- Collection in canisters or Tedlar® bags followed by direct injection onto the GC.
- (2) Chemical Characteristics of Groundwater. Groundwater samples must be analyzed to assess the presence and concentrations of target VOCs and associated chemicals, as well as the presence of potential IAS inhibitors. Chemical inhibitors of IAS include toxins that may impede the growth of microorganisms and subsequently the biodegradation rate. Additionally, inorganic compounds may precipitate when oxidized or excessive biomass may agglomerate, both of which can cause clogging of well screens. The presence of inhibitors does not necessarily preclude the application of IAS, but rather creates a potential operating problem which must be anticipated and accounted for in the IAS design.
- (a) Relatively high concentrations of iron (greater than 10 mg/L) may become oxidized and precipitate when aerobic IAS is implemented (EPA 1995a; Wisconsin DNR 1993; Marley and Bruell 1995). These documents advise that well screens may become clogged by precipated iron or by iron reducing bacteria, gradually reducing the subsequent ZOI of the IAS system. It has been observed, however, that fouling of IAS wells is rarely a problem, since sparge wells are essentially continuously being developed by the injected air. IAS has been conducted successfully at dozens of sites with high iron levels (D.H. Bass; Personal Communication, 1997). Where concerns remain, geochemical models, such as MINTEQA2 $^{\circ}$ , may aid in predicting the potential precipitation of iron and other dissolved metals detected in the subject aquifer, as well as buildup of iron bacteria at well screens. An additional discussion of biofouling is provided in paragraph 6-4(a).
- (b) Chemical groundwater parameters useful in assessing the feasibility of IAS are summarized in Table 3-2. Useful physical and biological property data are discussed in paragraphs 3-3a and 3-3c, respectively. Table 3-2 includes the preservatives required for the analytical methods referenced. Polyethylene or glass sample containers are used depending on the specific test parameter. Generally, 40-ml glass VOA vials with Teflon® septa are required for samples collected for VOC analyses. Standard SW 846 methods apply (USEPA 1986), as well as USACE guidance (EM 200-1-3).
- (c) Several methods are available for collecting groundwater samples. The methods typically implemented require either a semi-permanent sampling location, such as a groundwater monitoring well and low-flow, low-purge sampling (Puls and Barcelona 1996), or a temporary sampling location, such as can be accomplished using direct-push technology (DPT). DPT methods include Geoprobe®, Terraprobe®, MicroWell®, SimulProbe® and Hydropunch®, some of which are capable of being purged through inertial bailing and are therefore able to provide a representative sample of formation water at a point in the aquifer. DPT methods are typically used to yield chemical results from vertically discrete locations which can help develop a more accurate 3-dimensional "picture" of site contamination and geochemistry than generally available from groundwater wells. DPT groundwater sampling methods should be used in conjunction with soil sample collection to minimize sampling costs. However, semi-permanent groundwater monitoring wells are more cost-effective where groundwater is repeatedly sampled from the same location. The vertical

positioning of groundwater monitoring well screens (screened interval) should be carefully planned to ensure that the data obtained from a given well can be used to interpret the areal and vertical groundwater chemistry. Groundwater well screens are often 3 or more meters (10 or more feet) long. However, when wells with such long well screens are sampled, water can be collected from above or below the plume in addition to the water from within the plume. When this occurs, the resulting water quality measurements may reflect a mixture of clean oxygenated water with anaerobic contaminated water. Thus, the degree of oxygenation within the plume can be obscured. Consideration should be given to installing several nested wells with 0.6-meter (2-foot) well screens in such locations to maximize the resolution of the groundwater results.

- (d) It must be noted that IAS operational data (as opposed to site characterization data) acquired through monitoring wells may not represent true subsurface conditions (Johnson et al. 1993). Because of potential gas transfer within the well itself ("in-well aeration"), oxygen concentration measurements from the well may not be representative of the groundwater surrounding it. Figure 3-3 (Hinchee 1994) illustrates how air channeling to a monitoring well can cause the groundwater samples to have higher than representative DO and lower than representative VOC concentrations (Johnson et al. 1995).
- (e) In addition to dissolved groundwater contaminants, the presence or potential presence of NAPL must be assessed. NAPL can be present as either a light phase, less dense than water (LNAPL) or a heavy phase, more dense than water (DNAPL). Where both types of compounds are present at a site, mixtures of the two are common, and the tendency of the NAPL to float or sink depends on the density of the resulting mixture.
- (f) Because LNAPL and groundwater are immiscible fluids, LNAPL can be distributed within the capillary fringe above the groundwater table. LNAPL observed in a piezometer or monitoring well represents its apparent thickness. Several empirical and analytical relationships exist to convert the apparent thickness of LNAPL to the true thickness present in the subsurface formation (Testa and Paczkowski 1989; Farr et al. 1990; Lenhard and Parker 1990). Common parameters required to arrive at these relationships are listed below:
  - fraction of pore space in the formation, i.e., porosity
  - fraction of pore space occupied by LNAPL, i.e., oil saturation
  - specific gravity ratio of LNAPL to groundwater
  - fraction of the pore space occupied by recoverable LNAPL, defined as the difference between oil saturation and residual oil saturation
  - air/water capillary pressure-saturation relationship for the soil(s) of interest
- (g) Although some practitioners have observed LNAPL sites respond well to IAS, it is not likely to be successful if there is a significant volume of recoverable LNAPL. The utility of IAS in the presence of substantial layers of LNAPL is a matter of ongoing research.

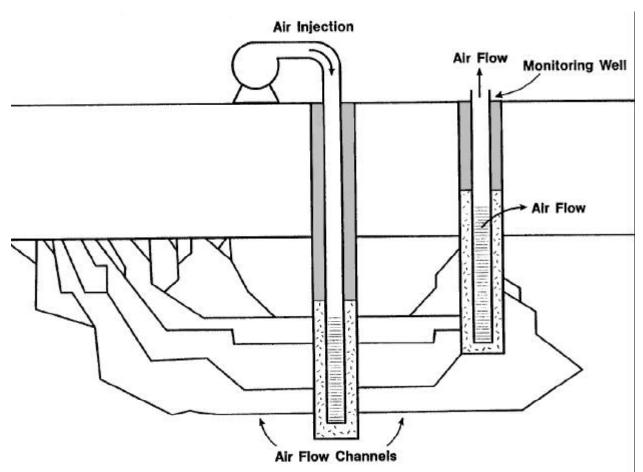


Figure 3-3. Cross section of IAS application illustrating air channeling to a monitoring well. (Hinchee 1994. Reprinted with permission from *Air Sparging for Site Remediation*. Copyright Lewis Publishers, an imprint of CRC Press, Boca Raton, Florida. ©1994.)

- (h) The extent and volume of LNAPL must be delineated prior to proceeding with IAS. The displacement that occurs during the startup of IAS systems may assist in upward mobilization of LNAPL trapped below the water table by groundwater fluctuations. It is generally recommended that free-phase LNAPL within an IAS ZOI be removed via a passive or active recovery system prior to the IAS system startup.
- (i) The extent to which the presence of DNAPL may impact the performance of IAS is uncertain. IAS may be useful in creating the subsurface agitation necessary to break up and dissolve pockets of DNAPL. However, identifying the presence of DNAPL prior to proceeding with IAS is not a trivial problem. DNAPL may significantly delay or impede the ability to achieve dissolved phase cleanup objectives. Additionally, IAS may potentially spread the immiscible liquid outside the ZOI or force it into deeper strata. For that reason, application of IAS to DNAPL-contaminated strata that overlie uncontaminated aquifer units is not recommended unless there is confidence that an intervening aquitard will prevent downward migration. Containment is generally the recommended approach for DNAPL sites that lack such an aquitard.
- (3) Chemical characteristics of soil Subsurface soil samples must be analyzed to assess the presence and concentrations of target VOCs and associated chemicals. For most soil strata impacted by hydrocarbons, the majority (often a large majority) of the hydrocarbon mass is sorbed to the soil particles or resides as NAPL within interstitial spaces. Soil concentrations provide the most useful assessment of how much material will actually require removal or degradation.
- (a) Chemical soil parameters useful in assessing the feasibility of IAS are listed below. Useful physical and biological property data are discussed in paragraphs 3-3a and 3-3c, respectively.
  - Specific VOC concentrations
  - Total Organic Carbon (or foc -- fraction organic carbon)
  - Ammonia-nitrogen
  - Total Kjeldahl nitrogen
  - Nitrite and nitrate
  - Ortho-phosphates
  - Total phosphates
  - Hq ●
  - Sulfates
  - Sulfides
- (b) Polyethylene or glass sample containers are used depending on the parameter of interest, and usually a temperature of less than  $4^{\circ}\text{C}$  must be maintained during transport. Generally, 4-oz wide-mouth glass jars with Teflon® septa are required for samples collected for soil VOC analyses, but in some cases, other glass containers may be acceptable. Standard SW-846 methods apply (USEPA 1986), as well as USACE guidance (EM 200-1-3).
- (c) Several methods are available for collecting soil samples. Analyses for chemical data do not typically require that the samples be undisturbed. However, VOCs are often lost through evaporation during

conventional soil sampling (Siegrist and Jenssen 1990; Hewitt 1994). A variety of sampling methods are available for the collection of undisturbed samples. Methods typically implemented include sample acquisition during borehole drilling, as well as DPT sampling devices. With these methods, it is imperative that samples be collected from depth-discrete intervals to differentiate among subsurface strata. For example, the groundwater interface may provide a more aerobic (i.e., oxygenated) environment than deeper strata.

- (d) Split-spoon samplers (generally 5-cm (2-inch) diameter, 60-cm (2-foot) length) are frequently used to collect depth-discrete samples while advancing hollow-stem augers in a borehole. DPT methods include Geoprobe®, Terraprobe®, SimulProbe®, and MicroWell®. These and other related DPT methods generate data of comparable quality to traditional methods (i.e., split-spoon samplers), but may not be as successful in recovering samples if the soil is very coarse, or if the sampling depth is >15 m (50 ft.). Cone penetrometers and sonication drilling rigs (e.g., Roto Sonic® drills, paragraph 3-3a(6)), by contrast, can produce soil characterization data to significantly greater depths. Use of the Triservice Site Characterization and Analysis Penetrometer System should also be considered.
- (4) Physical Properties of Chemicals. The physical properties of target chemicals detected in site media provide useful information related to the feasibility of IAS. The physical properties of chemicals not directly detected, but which could be created through oxidation, biodegradation, or other transformation processes, should also be identified. Physicochemical properties required for detected and potential chemicals are listed in Table 3-3.
- (5) Relationship among Chemicals. Chemical data can be used to assess the potential suitability of IAS. Field measurements of pH, dissolved oxygen, and redox potential in groundwater (shallow and deeper zones) are generally useful in assessing whether aqueous conditions tend to be aerobic or anaerobic, and the extent to which they vary with depth. Laboratory analyses of BOD and COD indirectly indicate the amount of biologically and chemically oxidizable material present. Elevated BOD and COD measurements indicate that a relatively elevated oxygen demand exists, either organic or inorganic in nature. If there is a significant amount of readily oxidizable material present that is non-target, then it may account for much of the oxygen uptake associated with IAS.
- (a) Laboratory analyses of nitrogen and sulfur compounds are useful in verifying whether subsurface conditions tend to be reductive or oxidative. Analyses of iron (total and field-filtered) further indicate the presence of either reductive or oxidative conditions.
- (b) Target organic chemicals (e.g., TCE) can be compared to concentrations of related compounds (e.g., cis- and trans-1,2-dichloroethene; VC). The presence of related compounds can be the result of releases of these compounds, impurities in the target compound, or natural subsurface transformation. Common transformation processes that can create related compounds include oxidation/reduction, biodegradation, hydrolysis, and elimination reactions.

TABLE 3-3
Useful Physicochemical Properties of Contaminants

Chemical's Physical Property	Typical Units	Significance
Molecular (formula) weight	g/mol	Chemicals tend to be more volatile as their molecular weight decreases.
Liquid density	g/cm <sup>3</sup>	Chemicals greater than or equal to 1 g/cm³ tend to form DNAPL if their solubility in water is exceeded; chemicals less than 1 g/cm³ tend to form LNAPL if their solubility in water is exceeded.
Vapor pressure	mm Hg	Chemicals greater than 1 mm Hg are considered volatile (USEPA 1995a).
Solubility in water	mg/L	The presence of NAPL should be suspected if aqueous concentrations exceed 1% of a chemical's solubility in water (Newell and Ross 1991).
Octanol/water partitioning coefficient (K <sub>ow</sub> )	dimensionless	A higher value indicates a chemical will preferentially dissolve in (partition into) an organic phase.
Organic carbon partitioning coefficient (K <sub>oc</sub> )	dimensionless	A higher value indicates a chemical will preferentially adhere to (partition into) organic material in soil. The extent of partitioning will depend upon the chemical's $K_{\rm oc}$ and the soil's foc. The more a chemical partitions into soil organic matter, the less effective IAS will be at stripping the chemical from the saturated zone.
Henry's law constant (K <sub>H</sub> )	atm-m³/mol or dimensionless	A higher value indicates a chemical will preferentially transfer from an aqueous to a gaseous phase. K <sub>H</sub> values greater than 2 x 10 <sup>-3</sup> atm-m <sup>3</sup> /mol are considered to indicate that IAS may work. IAS may not be appropriate for compounds with K <sub>H</sub> values less than 2 x 10 <sup>-3</sup> atm-m <sup>3</sup> /mol (EPA 1994). However, the success of biosparging is generally not dependent on K <sub>H</sub> values.

# TABLE 3-3 (Cont'd)

# **Useful Physicochemical Properties of Contaminants**

Chemical's Physical Property	Typical Units	Significance	
Redox potential <sup>1</sup>	volts	A higher value indicates a chemical will be reduced, rather than oxidized when coupled in a redox reaction.	
Notes:  1 Redox potential for a given oxidation/reduction half-reaction (e.g., Fe <sup>3+</sup> + e <sup>-</sup> Fe <sup>2+</sup> ).			

- (c) Combined with data obtained from biological analyses (paragraph 3-3c), the appropriate chemical data can be used to assess the nature and degree of microbial activity, and support the design of an appropriate IAS system.
- (6) Data Validation. Prior to using chemical data for decision-making purposes, some degree of data validation should be performed. In most cases, full validation in accordance with formal USEPA protocols is not required for site characterization or pilot-scale data related to the implementation of IAS (refer to EM 200-1-3). However, if comparisons to cleanup criteria are intended, full validation is recommended. At a minimum, data received from an analytical laboratory should be qualitatively assessed. Consideration should be given as to whether holding times and sample preservation requirements were met. A cursory review of chemicals detected in duplicates and blanks, as well as the percentage of surrogate recoveries in matrix spike samples, provide an indication of the quality of analytical data received. The Sampling and Analysis Plan (SAP) must include appropriate quality control samples, such as duplicates, matrix spikes, field and trip blanks at specified frequencies, usually as a percentage of the total number of samples collected.
- c. Evaluation of Bioremediation Feasibility. For most sites, the potential removal of organics by microbial degradation (e.g., biosparging) is dependent on a variety of factors, the most important of which are listed below. The order of importance will depend on the site specific conditions.
  - (1) Amenability of site contaminants to biodegradation
  - (2) Presence of microorganisms acclimated to the site contaminants
  - (3) Presence of toxic or inhibitory constituents (organic and inorganic)
- (4) Oxygen (or other electron acceptor) availability and/or ability to supply at needed rate
  - (5) Nutrient availability and/or ability to supply at needed rate
  - (6) Temperature
  - (7) pH
- d. The feasibility of biosparging is dependent on all of the same parameters as IAS (e.g., solubility, soil permeability, foc, soil homogeneity), except the contaminants' volatility. Contaminants that are amenable to biodegradation, but not volatile enough to consider stripping from saturated soil (e.g., naphthalene), may be treated by biosparging. Therefore, determination of the feasibility of biosparging requires the same assessment as for IAS with the assessment of the additional factors listed above.
- e. Microorganisms generally will utilize oxygen delivered via IAS until the hydrocarbons are no longer bioavailable. Therefore it may be more important to focus on how much oxygen can be delivered, and how well distributed it will be, than to determine degradation rates per se. The real utility of bench-scale biodegradation tests is to verify that there is no site condition that will limit or inhibit biodegradation.
- (1) Biodegradability. There have been numerous laboratory and field evaluations of the biodegradability of most common site contaminants. For

many light to medium weight fuel constituents (e.g., gasoline to #4 Fuel Oil), typical degradation rates are available in the literature. Published values are very site specific or may reflect a large range of degradation rates, and thus care should be used in extrapolating biodegradation rates for a given site. However, published values are useful for qualitatively assessing the feasibility of biodegradation at a site. The factors which can decrease the degradability of the constituents include concentration (e.g., due to toxicity effects), and time elapsed since contaminants were released into the environment. Typically after petroleum hydrocarbons infiltrate into the subsurface, the proportion of recalcitrant constituents will increase with time.

## (2) Bacterial Population Densities.

- (a) The presence of a high population density of bacteria in contaminated saturated soil is generally indicative of conditions that can accommodate bioremediation. However, small population densities of bacteria do not necessarily indicate that bioremediation is infeasible, but rather that existing conditions are not favorable for promoting bacterial growth. If there are low bacterial population densities, it is important to consider whether there are subsurface conditions, limiting bacterial activity, that may be manipulated during remediation. For example, in an aquifer contaminated with petroleum, there may be little or no dissolved oxygen (i.e., < 2 ppm) and relatively low population densities of aerobic heterotrophic (organic carbon metabolizing) bacteria and aerobic contaminant-specific degrading bacteria. However, upon introduction of dissolved oxygen through biosparging, population densities of aerobic bacteria may increase rapidly and provide the means for biodegrading the petroleum contaminants. Similarly, an aquifer lacking another limiting nutrient such as available nitrogen may have relatively low population densities of bacteria but may be suitable for bioremediation if growth is stimulated by delivering this nutrient.
- (b) Comparison of bacterial population densities of background and contaminated zones provides additional insight into the feasibility of bioremediation. If there are significantly greater numbers of either heterotrophic or specific contaminant degraders present in the contaminated zone, then there is evidence that the bacteria in the contaminated zone may be capable of biodegrading some (or all) of the contaminants. Again, the converse does not necessarily demonstrate that bioremediation is infeasible, but that there may be some factor inhibiting bacterial growth.
- (c) There are a variety of methods for estimating the population densities of both total heteroptrophic and specific contaminant degrading subsurface microbes, including: plate counts, Most Probable Number (MPN), phospholipid fatty acid analysis, enzyme activity analysis, and ATP bioluminescence assays. Plate counts and MPN methods are the most frequently used.
- (d) With plate counts, site soil is added to nutrient rich agar medium in Petri dishes, incubated, and then the number of separate colonies grown (Colony Forming Units or CFU) are counted. Plate counts of specific contaminant degraders (i.e., native bacteria that can use the contaminant as a sole source of carbon) use a medium containing one or more of the organic

contaminants, such as gasoline or naphthalene as the sole carbon source. When population densities are estimated by plate counts, they are typically expressed as exponential numbers, such as  $2 \times 10^6$  CFU/g-soil. MPN tubes are the most common alternative to plate counts. Site soil is added to tubes of media in which growth can be detected by color change, gas generation, turbidity, or other means. The numbers from these two methods are not directly comparable (i.e.,  $5 \times 10^5$  CFU/g is not the same as  $5 \times 10^5$  MPN/g).

- (e) Various laboratories and companies who specialize in bioremediation have laboratory methods to conduct these tests. There are accepted standard methods for sewage and water quality (APHA/AWWA/WEF 1992) but not universally accepted methods for wastes and hazardous wastes. Methods shown in the above reference may be modified for environmental remediation purposes, and such modified methods may be used to assess microbial activity. Methods of Soil Analysis, Part 2 Chemical and Microbiological Properties, 2nd Edition (Page et al. 1982) also includes methods for microbial activity testing. The results of these tests are most meaningful in comparison with other results from the same site to indicate the potential to use IAS to enhance biodegradation.
  - (f) The methods and typical expectations are presented in Table 3-4.
  - (3) Laboratory Biodegradation Tests.
- (a) In addition to testing soil and/or groundwater samples to monitor microbial activity, laboratory tests may be used to evaluate the feasibility of bioremediation. Biodegradation rates may also be measured under controlled, laboratory conditions. For contaminants that consistently have been demonstrated to be biodegradable, such as gasoline, laboratory biodegradation tests are generally unnecessary. However, possible reasons for performing these tests for known-to-be biodegradable contaminants include:
  - determination of the presence of a toxic constituent in the soil;
  - identification of mineral nutrient limitations (e.g., nitrogen or phosphorus); or
  - demonstration that the proposed treatment approach is viable.
- (b) Biodegradation tests are also useful for evaluating contaminants whose biodegradability is unknown, or which are recognized to be biodegradable but are considered to be recalcitrant. Two common laboratory degradation tests are shake flask tests and respirometry tests. Shake flask tests are generally performed on a slurry of site soil in site groundwater and measure the rate of disappearance of the contaminant under controlled conditions. Respirometry tests measure oxygen utilization and carbon dioxide production.
- (c) Shake flask or microcosm tests are usually comprised of a series of flasks, usually at <25 % solids, that are subject to different test conditions which test the impacts of various amendments and other parameters on the degradation process. The flasks are shaken or stirred to provide aeration and mixing. This approximates the addition of air to the subsurface. If nutrient amendment is being considered, then the nitrogen and phosphorus levels in the soil and groundwater may be used to determine the levels of nutrients to add (e.g., Ward et al. 1995).

TABLE 3-4
Microbiological Tests and Typical Results

Test Description	Typical Initial Results	Typical Highest Results	Comments
Total Heterotrophic Bacteria (Plate or MPN)	1,000 - 10,000 (10³ - 10⁴) CFU/g	10 <sup>8</sup> - 10 <sup>10</sup> CFU/g	Microbes which use organic carbon
Hydrocarbon Degraders (Plate or MPN)	1000 - 10,000 (10³ - 10⁴) CFU/g	10 <sup>6</sup> - 10 <sup>8</sup> CFU/g	Microbes which use the target range of hydrocarbon compounds
Specific Compound Degraders	100 - 1,000 (10 <sup>2</sup> - 10 <sup>3</sup> ) CFU/g	10 <sup>5</sup> - 10 <sup>6</sup> CFU/g	Microbes which use specific target compounds (e.g. naphthalene)

- (d) A typical test matrix is shown in Table 3-5. Since the subsurface will be aerated in all cases, an anaerobic control may not be necessary in assessing biosparging.
- (e) If the soil water pH is not in the range of 6-8 standard units, the pH may be adjusted to this range as another test condition.
- (f) These tests are conducted on identically prepared flasks for each test condition, with sufficient flasks to perform testing at 0, 3, 7, 14, 28 and sometimes additional days from study initiation. Usually duplicates are prepared so that additional statistical sampling may be conducted on some of the data. The flasks are sacrificed and tested for the contaminant concentrations in the soil and water phases at the specified time intervals, and decay curves are calculated to derive an approximate degradation rate under laboratory conditions. The abiotic control provides an indication of the amount of phase transfer which occurs in the absence of biodegradation, so the degradation rate can be appropriately adjusted.
- (g) These tests are generally conducted at ambient indoor temperatures, not groundwater temperatures. In-situ biodegradation rates may be slower because the subsurface will generally be colder than the laboratory test conditions, and groundwater will not be as well mixed as in the laboratory.
- (h) These shake flask tests provide a basic indication as to whether the site conditions are favorable, or can be made favorable, for the indigenous organisms to degrade the organic materials at the site. For longer tests, they may provide an indication of the maximum removal which might be achieved at the site using biosparging. Such data may be useful for establishing a lower limit cleanup level for contaminants of concern. However, the lower limit observed in the laboratory will probably be below the concentration that should be expected in-situ.
- (i) Rather than (or in addition to) monitoring concentrations of contaminants, respiration tests may be used to monitor microbial activity. A respiration test may entail measuring the rate of oxygen disappearance (uptake) as degradation proceeds. A degradation rate can then be calculated based on the uptake rate. Another variation uses the generation rate of carbon dioxide to perform a similar calculation. Both of these approaches must be evaluated with respect to abiotic sources and sinks for oxygen and carbon dioxide. In the oxygen uptake case, reduced iron may compete with bacteria for oxygen. For carbon dioxide generation, inorganic carbonate may act as a source or sink of carbon dioxide. Monitoring both oxygen uptake and carbon dioxide generation can help to clarify these confounding influences. Extended respirometry tests require a source of oxygen into the test apparatus at a controlled rate to insure an adequate supply in the closed system. However, batch tests may also be performed using only a probe to monitor dissolved oxygen, in solution. Respirometry tests may be less expensive than other laboratory biodegradation tests.

TABLE 3-5

Typical Degradation Test Matrix\*

Test Conditions	Additives	Comments
Native conditions (air only)	None (slurry only)	Background
Nutrients at dosage 1	Ammonia-nitrogen, phosphate	Nutrient amended
Nutrients at dosage 2	Ammonia-nitrogen, phosphate	Nutrient amended
Abiotic control	Sodium azide, HgCl, or other microbial poison	Determine non- microbial effects
Duplicate of at least one condition above	Match above additives	Establish crude statistical basis

<sup>\*</sup>At some sites, other matrices may be appropriate that do not include nutrient amended test conditions.

## 3-4. <u>Feasibility Studies</u>.

- a. Generally the feasibility study is a combination of the physical, chemical and biological evaluations described in the previous sections, and leads to a pilot test of some form if the technology still appears promising. At some sites, certain components of a feasibility study can be dispensed with because they are not necessary. For example, if the biodegradability of the contaminants of concern has already been established, (e.g., sites with jet fuel contamination), the decision may be made to forego all or part of the bioremediation evaluation. Although laboratory column studies simulating IAS can be instructive in elucidating airflow mechanics (e.g., Ji et al. 1993), they are generally not justified as part of a feasibility study because they are not likely to be representative of the larger scale of the site.
- b. A part of the feasibility study is an economic evaluation of the likely cost to test and implement IAS, in comparison to other technologies. Most feasibility studies recommend the technology which is likely to attain the cleanup goals for the site at minimum cost. For an in-situ technology such as IAS, this cost of treatment is very site specific, and is primarily affected by the concentration and mass of hydrocarbon to be treated, the depth of the plume and its relationship to the water table depth, the areal extent of the plume to be treated, and the ZOI which can be generated and maintained in the formation.
- c. Another approach that may especially be applicable to small sites, can include performance of a limited pilot study in the initial phases of a project. Such a test may cost effectively demonstrate the feasibility or infeasibility of IAS, and may be considered a prequalification test (paragraph 4-3c).
  - d. Pilot Test methods and guidance will be provided in Chapter 4.